

A $\delta^{13}\text{C}$ and $\delta^2\text{H}$ leaf wax record from the Late Quaternary loess-paleosol sequence El Paraíso, Central Spain

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ABSTRACT

The Mediterranean Peninsula increasingly suffers from droughts and aridity, the first consequences of global climate change in that region. Precise scenarios for the region's future climate predictions require knowledge about the processes of past climate changes, but information about the Western Mediterranean climate and its history is controversial. For this study, we applied compound-specific $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses on long-chain *n*-alkanes in the ~8 m El Paraíso loess-paleosol sequence (LPS), Central Spain, to investigate climate and environmental changes during the Late Quaternary. The $\delta^{13}\text{C}$ values are most enriched during marine isotope stage (MIS) 3, indicating more arid conditions, while lower values during MIS 4 and 2 are interpreted to document more humid conditions. Low values are also recorded for the Holocene colluvium, which can at least partly be explained with higher concentrations in atmospheric CO_2 . The $\delta^2\text{H}$ values are mostly enriched during the last glacial compared to the Holocene. We suggest that this is mainly controlled by isotopic effects related to the moisture source, yet other possible effects like evapotranspirative enrichment and changes in atmospheric circulation patterns shouldn't be ruled out. Our results corroborate previous findings based on leaf wax patterns, geomorphological records, and climate models. They all indicate relatively humid conditions during MIS 2 compared to more arid phases during MIS 3.

1. Introduction

The Iberian Peninsula increasingly suffers from the first consequences of the current global warming (Giorgi and Lionello, 2008; Seager et al., 2014). For precise predictions and to better anticipate the environmental impacts of future climate change on the Western Mediterranean, it is crucial to understand past climate and environmental changes. The region's climate is mainly controlled by the North Atlantic atmospheric circulation system (westerly storm tracks), whose positions and strengths varied over the last glacial/interglacial cycles (Florineth and Schlüchter, 2000). Since the recent global climate change affects the global atmospheric circulation patterns, westerlies tend to shift more northwards, leading to an enhanced aridization on the Iberian Peninsula (Giorgi and Lionello, 2008). However, based on its specific orographic situation, the Iberian Peninsula displays highly varying

physiographic conditions and precipitation trends may show strong regional differences (Hidalgo-Muñoz et al., 2011; Martin-Vide and Lopez-Bustins, 2006). Therefore, it is all the more important to study the effects of global climate changes on terrestrial environments in a defined regional context (Faust and Wolf, 2017). So far, relevant paleoclimate information for the Iberian Peninsula comes from various archives (e.g. lakes, peat bogs, glacial landforms, loess paleosol sequences) and proxies (e.g. geomorphological reconstructions, pollen), but findings are controversial, especially regarding moisture conditions during marine isotope stage (MIS) 2. Pollen records indicate more arid conditions (e.g. Carrión et al., 2010; González-Sampériz et al., 2006), while reconstructions of lake levels and glacier extents, and paleoclimate models show more humid conditions especially after 28 ka (Beghin et al., 2016; Domínguez-Villar et al., 2013; Moreno et al., 2012, 2014b; Prentice et al., 1992). To drive this issue forward is a main

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objective of the study in hand.

In a previous study (Schäfer et al., 2016), we have analysed the leaf wax patterns (long-chain *n*-alkanes and *n*-alkanoic acids) in the ~8 m thick El Paraíso loess-paleosol sequence (LPS) in Central Spain to contribute to the reconstruction of the vegetation and climate history in inner Iberia during the Late Quaternary. The leaf wax patterns indicated a dominance of grass-derived lipids for nearly the whole profile, yet more contributions from deciduous trees during MIS 2, which we have interpreted to document more humid conditions.

The analysis of the stable carbon and hydrogen isotopic composition of leaf wax derived *n*-alkanes (δ_{wax}) is a relatively new approach to reconstruct paleoclimatic and paleohydrological changes (e.g. Collins et al., 2013; Vogts et al., 2012; M. Zech et al., 2013; R. Zech et al., 2013). *n*-Alkanes are often the most abundant lipids in soils and sediments, because they are very stable over geological time scales (Eglinton and Eglinton, 2008). At low temperatures, they do not show an exchange of carbon and hydrogen during degradation and pedogenesis (Schimmelmann et al., 1999). The $\delta^{13}\text{C}$ signal of leaf waxes can be used to distinguish between C_3 vs. C_4 vegetation (Rommerskirchen et al., 2006) with C_3 plants showing lower values (–23 to –34‰) compared to C_4 plants (–6 to –23‰, Schidlowski, 1987). C_4 plants are more competitive than C_3 plants when the atmospheric CO_2 concentration is low, i.e. during glacial times. Additionally, the $\delta^{13}\text{C}$ -value of leaf wax *n*-alkanes depends on the $\delta^{13}\text{C}$ of the atmospheric CO_2 , as well as on its concentration, air temperature, relative humidity and precipitation during the growing season (e.g. Diefendorf et al., 2010).

The $\delta^2\text{H}$ -values of leaf waxes reflect the isotopic signal of the precipitation $\delta^2\text{H}_{\text{precip}}$, which depends mainly on the isotopic composition of the moisture source, but is also influenced by the temperature, amount, continentality, and altitude effect (Berke et al., 2015; Sachse et al., 2012; Tipple et al., 2013). The biosynthetic fractionation can vary depending on plant type and environmental conditions (e.g. Sachse et al., 2012; Berke et al., 2015), but for paleoenvironmental studies these variations are generally assumed to be less important and hence, the biosynthetic fractionation is treated as constant in several studies (Niedermeyer et al., 2016; R. Zech et al., 2013; Sachse et al., 2012). However, evapotranspirative enrichment of leaf water, and thus leaf waxes, needs to be taken into consideration when interpreting leaf wax $\delta^2\text{H}$ records (Kahmen et al., 2013; Tuthorn et al., 2015; Zech et al., 2015).

The aim of the present study was to apply compound-specific $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses on the long-chain *n*-alkanes from the El Paraíso LPS. This is a pilot study to

- evaluate the potential of coupling compound-specific $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses on leaf waxes, and,
- further contribute to the paleoclimate and –environmental reconstruction in Iberia during the last glacial, which is even more meaningful since terrestrial paleoclimatic archives that provide information about the last glacial in inner Iberia are extremely rare.

2. Material and methods

2.1. Climate setting

The Iberian Peninsula's climate is influenced by the North Atlantic and the western Mediterranean circulation system. Winter precipitation is dominated by the North Atlantic moisture source that is commonly considered to depend on the state of the North Atlantic Oscillation (NAO, Moreno et al., 2014a). In a positive phase of the NAO, westerlies are stronger at higher latitudes and more arid conditions prevail over Southern Europe (Fig. 1a, blue line). During a negative phase, the westerlies shift southwards. Moisture is transported to Southern Europe where more humid conditions with enhanced winter precipitation occur (Fig. 1a, orange line, Bojariu and Gimeno, 2003). Over the past 30 years, a trend to a more positive phase of the NAO has been observed

(Visbeck et al., 2001 and references therein), resulting in more arid winters over the Western Mediterranean (Folland et al., 2002).

The summer precipitation regime is mainly controlled by the Western Mediterranean Oscillation (WeMO, Moreno et al., 2014a). In a positive phase of the WeMO, enhanced westerlies provide summer precipitation for the whole Iberian Peninsula, but they are not able to transport moisture all along to the east coast, which results in an enhanced summer aridity gradient from west to east Iberia (Martin-Vide and Lopez-Bustins, 2006). During a negative phase of the WeMO, wind systems from the Mediterranean Sea transport moisture over the Iberian Peninsula leading to more humid summers in the east (Fig. 1b).

The nearest weather station to our research site shows the pronounced seasonality typical for the Mediterranean climate (station Aranjuez, Fig. 1c). The highest temperatures during summer coincide with lowest rainfall, resulting in seasonally very dry climate conditions. Annual rainfalls are moderate (400–500 mm) and mean annual temperatures are between 11 and 14 °C. $\delta^2\text{H}_{\text{precip}}$ also shows a pronounced seasonal pattern. Values are lowest in winter and highest during summer.

2.2. Research site and sampling

The El Paraíso LPS (560 m a.s.l., N 40° 01.855', W 03° 28.031') is located in Central Spain, south of Madrid in the Tagus River valley (Fig. 1a). It exposes up to 8 m of loess, loess-like sediments and slope deposits and comprises several loess units and fossil soils (Fig. 1d). Age control for the profile is based on optically stimulated luminescence (OSL) and radiocarbon dating and is presented in detail together with a stratigraphical, sedimentological and paleo-pedological discussion of other loess sections from that region in Wolf et al. (2018). The late Pleistocene portion of the Paraíso section that is located 50 m above the recent river bed, the first sediment unit (SU-3) consists of relocated marl material that rests on bedrock (SU-1, gypsum marl) (Fig. 2). The middle and upper parts of the sections are characterized by the incorporation of loess material. A first phase of loess deposition (SU-4) took place during MIS 5, as indicated by OSL dating results. After a period of stability and intense soil formation, a first accumulation of pure aeolian loess took place in a period around 64.1 ± 6.0 kyr and 59.7 ± 4.7 kyr (SU-5). According to dating results, the next phase of loess deposition (SU-6) occurred around 43.0 ± 3.8 kyr and 42.5 ± 3.6 kyr during the middle MIS 3. Thereafter, another prominent phase of loess deposition (SU-7) took place around 30.5 ± 2.4 and 31.2 ± 2.4 kyr at the end of MIS 3, replacing a prolonged period of stability. The last period of loess deposition in the Paraíso section took place around 25.9 ± 2.4 kyr (SU-8) (Fig. 2). The uppermost unit (SU-10) consists of colluvial slope deposits and indicates strong sediment shifting most likely related to very recent human land use practices (for further details on dating results we refer to Wolf et al., 2018).

2.3. Laboratory methods

Total lipid extraction and separation into lipid fractions is described in Schäfer et al. (2016). The aliphatic fraction containing the *n*-alkanes was used for compound-specific stable isotope analyses. Some samples had to be further purified before these measurements due to coeluting compounds. For that, we used pipette columns filled with silica gel impregnated with activated AgNO_3 to retain the unsaturated compounds, and pipette columns filled with zeolite (Geokleen) to retain the straight chain saturated compounds. After drying, the zeolite was dissolved in HF, and the *n*-alkanes were recovered by liquid-liquid extraction with hexane.

The compound-specific carbon isotope measurements were performed on an IsoPrime 100 mass spectrometer, coupled to an Agilent 7890A GC via a GC5 Pyrolysis/Combustion interface that operated in combustion mode (CuO reactor) at 850 °C. Samples were injected using a split/splitless injector in splitless mode. The GC was equipped with a

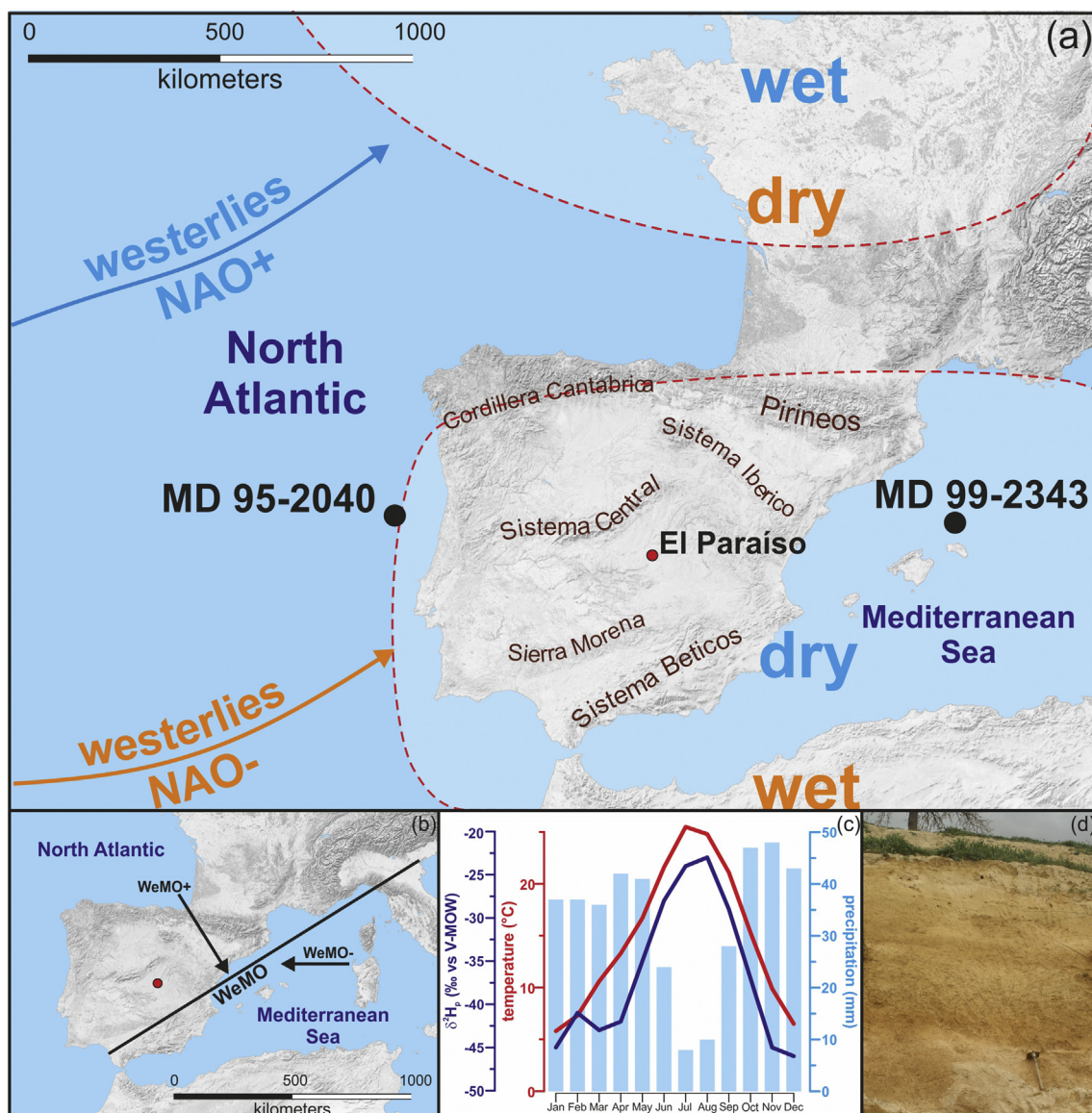


Fig. 1. (a) Location of the sampling site (sources: Esri, USGS, NOAA) and position of the westerlies during a positive (blue) and negative (orange) phase of the North Atlantic Oscillation (NAO) with extension of dry/wet climate conditions (adapted from Bojariu and Gimeno, 2003). (b) Positive and negative phase of the Western Mediterranean Oscillation (WeMO). Black arrows indicate direction of moisture advection (after Martin-Vide and Lopez-Bustins, 2006). (c) Climate diagram of Aranjuez, the station nearest to our sampling site (source for climate data: <http://www.weatherbase.com>. Source for $\delta^2\text{H}$ -values of precipitation: OIPC, version 3.0, Bowen, 2017; Bowen et al., 2005). (d) Photograph of the profile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

30 m fused silica column (HP5-MS, 0.32 mm i.d., 0.25 μm film thickness). Precision of the measurements was checked by injecting a standard alkane mix (C_{27} , C_{29} , C_{33}) with known isotopic composition twice every six injections. The analytical error of standards and samples was 0.2‰ (triplicate measurements). The stable carbon isotope composition is given in the delta notation ($\delta^{13}\text{C}$) versus Vienna Pee Dee Belemnite (V-PDB).

For the compound-specific hydrogen isotope measurement, the GC5 mode was changed to pyrolysis by using a Cr (ChromeHD) reactor at 1000 °C. GC settings remained the same as for the stable carbon isotope measurements. The H_3^+ -correction factor was checked every two days and was stable at 3.48 ± 0.06 . The analytical error of standards and samples was 2.3‰ (triplicate measurements). For data interpretation, we report only values with a standard deviation better than 6‰. The stable hydrogen isotope compositions are given in the delta notation ($\delta^2\text{H}$) versus Vienna Standard Mean Ocean Water (V-SMOW).

3. Results

3.1. $\delta^{13}\text{C}_{\text{wax}}$

Concentrations of the most abundant compounds, $n\text{-C}_{29}$ and $n\text{-C}_{31}$, were sufficient ($\geq 50 \text{ ng}/\mu\text{l}$ per target compound) for compound-specific $\delta^{13}\text{C}$ analyses in all samples (Fig. 2 and Table 1). In most samples, the $n\text{-C}_{29}$ alkane is $\sim 1\%$ more enriched than the $n\text{-C}_{31}$ alkane. This is in agreement with observations from other studies, which reported a trend to more negative values with increasing n -alkyl chain length (Oppermann et al., 2010 and references therein). The $\delta^{13}\text{C}$ values of $n\text{-C}_{29}$ in the lowermost samples increase slightly from $-33.1 \pm 0.2\text{‰}$ to $-30.6 \pm 0.2\text{‰}$ during MIS 5 and the early MIS 4 but drop back to low values of $\sim -32.3 \pm 0.2\text{‰}$ during later stages of MIS 4. $\delta^{13}\text{C}_{29}$ increases again during MIS 3, reaching values of $-28.3 \pm 0.2\text{‰}$ at 4.56 and $-27.7 \pm 0.1\text{‰}$ at 3.54 m depth. Towards the MIS 3/2 transition at $\sim 2 \text{ m}$ depth, a trend to values as low as $-32.4 \pm 0.2\text{‰}$ can be

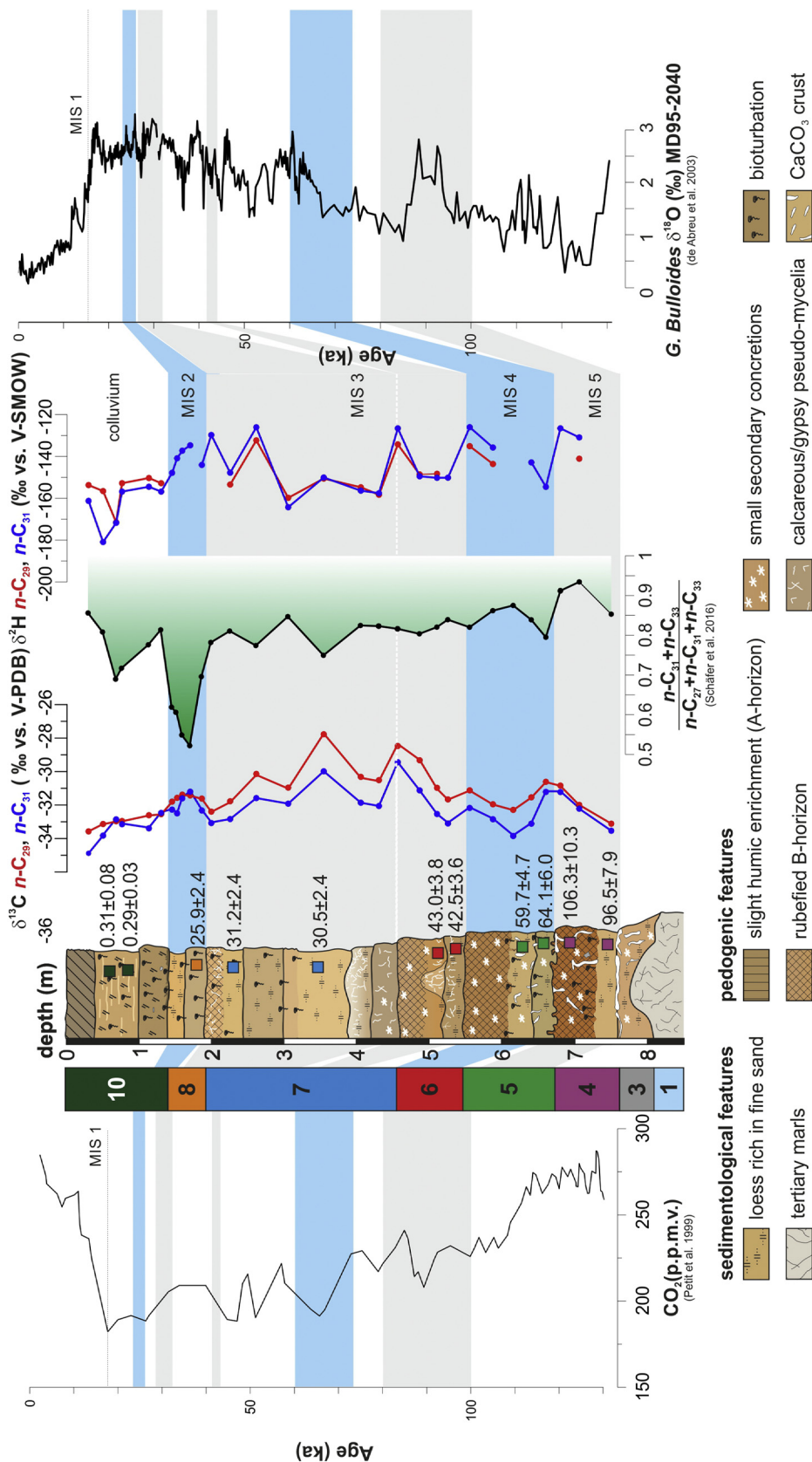


Fig. 2. δ_{vax} proxies in the El Paraíso LPS. From left to right: atmospheric CO₂ concentration during the Late Quaternary (Pett et al., 1999), δ¹³C-values of the most abundant *n*-alkane compounds *n*-C₂₉ (red) and *n*-C₃₁ (blue), *n*-alkane ratio (*n*-C₃₁ + *n*-C₃₃)/(*n*-C₂₇ + *n*-C₃₁ + *n*-C₃₃) used to distinguish between the input of deciduous trees vs. grasses and δ²H-values of *n*-C₂₉ (red) and *n*-C₃₁ (blue) in the El Paraíso LPS, and comparison between the δ¹⁸O record of the planktonic foraminifera *G. bulloides* from marine drill cores MD95-2040 in the North Atlantic (de Abreu et al., 2003). Gasps in the isotopic curves are due to insufficient target concentrations of the specific compounds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

$\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of the most abundant compounds $n\text{-C}_{29}$ and $n\text{-C}_{31}$ with standard deviation (Std dev) of the three replicate measurements. Where no values are reported the standard deviation was higher than 6‰ or the target compounds were too low in concentration for reliable analyses.

Sample	Depth	MIS	$\delta^{13}\text{C}_{\text{C}_{29}}$	SD C_{29}	$\delta^{13}\text{C}_{\text{C}_{31}}$	SD C_{31}	$\delta^2\text{H}_{\text{C}_{29}}$	SD C_{29}	$\delta^2\text{H}_{\text{C}_{31}}$	SD C_{31}
PA57	0.30	MIS 1	−33.6	0.1	−34.9	0.2	−153.7	4.0	−161.3	1.2
PA56	0.50		−33.1	0.3	−33.8	0.2	−156.6	1.3	−181.0	3.9
PA55	0.68		−33.0	0.2	−32.9	0.7	−171.5	1.2	−171.8	1.9
PA54	0.76		−33.0	0.1	−33.1	0.3	−152.8	0.6	−156.8	2.4
PA53	1.13		−32.6	0.4	−33.4	0.1	−150.3	3.7	−154.5	1.3
PA52	1.30	MIS 2	−32.5	0.5	−32.5	0.2	−152.8	0.6	−156.8	2.4
PA51	1.45		−31.8	0.1	−32.3	0.2	–	–	−147.9	5.9
PA50	1.52		−31.6	0.4	−32.5	0.2	–	–	−140.9	2.0
PA49	1.59		−31.4	0.1	−31.6	0.2	–	–	−137.3	4.7
PA48	1.70		−31.4	0.1	−31.2	0.7	–	–	−134.7	1.6
PA47	1.77	MIS 3	−30.8	0.1	−31.6	0.2	–	–	–	–
PA46	1.86		−31.6	0.2	−32.3	0.2	–	–	−144.1	4.6
PA45	1.99		−32.4	0.2	−33.1	0.1	–	–	−129.8	4.5
PA43	2.25		−31.8	0.1	−32.9	0.1	−153.5	1.9	−147.8	1.9
PA41	2.61		−30.2	0.2	−31.6	0.5	−132.3	1.9	−126.1	2.5
PA39	3.05	MIS 4	−31.0	0.1	−32.0	0.0	−159.8	1.2	−164.3	1.6
PA36	3.54		−27.7	0.1	−30.0	0.1	−150.6	0.8	−150.1	0.5
PA33	4.05		−30.4	0.1	−31.9	0.1	−154.8	2.6	−156.4	3.5
PA31	4.30		−30.6	0.1	−32.1	0.2	−158.4	2.7	−157.6	3.5
PA29	4.56		−28.3	0.2	−29.5	0.2	−134.2	3.3	−126.6	2.6
PA27	4.86	MIS 5	−29.3	0.1	−31.2	0.2	−148.6	0.1	−149.5	4.8
PA25	5.10		−31.0	0.2	−32.6	0.1	−148.3	2.1	−150.2	2.9
PA24	5.25		−31.7	0.3	−33.1	0.1	–	–	−150.2	5.4
PA22	5.55		−31.1	0.4	−32.2	0.2	−135.1	2.7	−126.0	3.0
PA20	5.87		−32.0	0.3	−32.8	0.2	−143.7	1.7	−135.7	1.5
PA18	6.15	MIS 5	−32.3	0.2	−33.9	0.4	–	–	–	–
PA16	6.40		−31.5	0.3	−33.1	0.2	–	–	−142.9	3.6
PA14	6.60		−30.6	0.2	−31.2	0.1	–	–	−154.6	0.2
PA12	6.80		−30.8	0.2	−31.2	0.2	–	–	−126.6	2.4
PA09	7.06		−32.0	0.1	−32.2	0.1	−141.1	1.3	−130.9	2.1
PA05	7.50		−33.1	0.2	−33.5	0.0	–	–	–	–

observed. Low values of $\sim -31.5 \pm 0.1\text{‰}$ also characterize MIS 2, before the trend to more negative $\delta^{13}\text{C}$ values continues in the Holocene colluvium starting with $-32.5 \pm 0.5\text{‰}$ and ending with $-33.6 \pm 0.1\text{‰}$.

3.2. $\delta^2\text{H}_{\text{wax}}$

Most, but not all samples contained sufficient amounts of target compounds ($\geq 300 \text{ ng}/\mu\text{l}$ per target compound), again $n\text{-C}_{29}$ and $n\text{-C}_{31}$, to obtain robust $\delta^2\text{H}$ results (Fig. 2 and Table 1). Gaps in Table 1 and Fig. 2 are due to concentrations lower than the sufficient target amounts needed for reliable compound specific $\delta^2\text{H}$ data of the respective compounds. The trends of the depth curves are similar for $n\text{-C}_{29}$ and $n\text{-C}_{31}$ whereas the specific values of both compounds can deviate by $\sim 7\text{‰}$ in the same sample. During MIS 5, the $\delta^2\text{H}$ values of $n\text{-C}_{31}$ increase from $-130.9 \pm 2.1\text{‰}$ to $-126.6 \pm 2.4\text{‰}$. In the lowermost sample belonging to MIS 4, the values are as low as $-154.6 \pm 0.2\text{‰}$ and increase to a maximum of $-126.0 \pm 3.0\text{‰}$ at the top of the sediment unit. During MIS 3, values vary without an obvious discernible pattern and get as low as $-164.3 \pm 1.6\text{‰}$ in 3.05 m depth and as high as $-126.1 \pm 2.5\text{‰}$ in 2.61 m depth. A trend to more depleted values becomes recognizable during MIS 2 ranging from $-134.7 \pm 1.6\text{‰}$ in 1.7 m depth to $-147.9 \pm 5.9\text{‰}$ in 1.45 m depth. In the Holocene colluvial deposit, values vary widely from $-154.5 \pm 1.3\text{‰}$ in 1.13 m depth to $-181.0 \pm 3.9\text{‰}$ in 0.5 m depth.

4. Discussion

4.1. Paleoclimatic interpretation of $\delta^{13}\text{C}_{\text{wax}}$

The curve of the $\delta^{13}\text{C}_{\text{wax}}$ -signal in the El Paraíso LPS shows a distinctive course over the last glacial/interglacial cycle starting from more depleted values at the base of the profile (MIS 5 and 4), reaching

more enriched values in the middle part (MIS 3), and finally going back to lower values in the uppermost part (MIS 2 and 1). Nearly all the $\delta^{13}\text{C}_{\text{wax}}$ -values are in the range of published C_3 plant waxes (-29 to -39‰ , Bi et al., 2005; Collister et al., 1994, Table 1). Thus, it is conceivable that, if at all, C_4 plants only had reduced influence on the enrichment of the $\delta^{13}\text{C}_{\text{wax}}$ signal in our record.

Another factor that can lead to variations in $\delta^{13}\text{C}_{\text{wax}}$ is the fluctuation in the $\delta^{13}\text{C}$ -value of the atmospheric CO_2 . However, it is known that the $\delta^{13}\text{C}$ composition of $\text{CO}_{2\text{atm}}$ did not change strongly during the last glacial (Leuenberger et al., 1992).

The concentration of atmospheric CO_2 (pCO_2) can also influence $\delta^{13}\text{C}_{\text{wax}}$ (Feng and Epstein, 1995; Schubert and Jahren, 2012). An increase in pCO_2 results in a stronger discrimination against ^{13}C during plant lipid synthesis. Thus, higher concentrations during interglacial stages can lead to $\delta^{13}\text{C}_{\text{wax}}$ -values that are depleted by $\sim 2\text{‰}$ compared to glacial stages (Zech et al., 2007 and references therein). The transition from MIS 2 to the Holocene colluvium in the El Paraíso LPS is indeed accompanied by a decrease in $\delta^{13}\text{C}_{\text{wax}}$ in the range of $\sim 1\text{–}2\text{‰}$ (Table 1, Fig. 2), which can be the consequence of the increase in pCO_2 . Additionally, $\delta^{13}\text{C}_{\text{wax}}$ can depend on the plant growth form with $1\text{–}2\text{‰}$ more enriched $\delta^{13}\text{C}$ biomass in grasses than in other growth forms (Arens et al., 2000). As the transition from MIS 2 to the Holocene involves the end of the glaciation, a change in the vegetation composition as reason for changes in $\delta^{13}\text{C}_{\text{wax}}$ needs to be considered. However, based on the vegetation reconstruction from the leaf wax derived sedimentary n -alkanes, the proportion of deciduous trees decreased relative to the amount of grasses rather than it increased from MIS 2 to the Holocene (Fig. 2 and Schäfer et al., 2016). This pattern contradicts a strong influence of vegetation changes on $\delta^{13}\text{C}_{\text{wax}}$.

Variations of $\delta^{13}\text{C}_{\text{wax}}$ in the LPS during the MIS 5 could also be explained by variations in pCO_2 . The loess package from 6.8 to 7.5 m depth was probably deposited during a relatively short time period in the early to middle MIS 5. The soil development then occurred until

MIS 5a where the atmospheric CO₂ curve shows a general trend to lower concentrations (Fig. 2). Hence, the trend to more enriched $\delta^{13}\text{C}_{\text{wax}}$ values related to the soil formation in SU-4 (middle to late MIS 5) compared to the $\delta^{13}\text{C}_{\text{wax}}$ values of the parent material (lower SU-4) probably reflects the decrease in atmospheric pCO₂.

The $\delta^{13}\text{C}_{\text{wax}}$ -variations during MIS 4, MIS 3 and MIS 2 in the profile do not correlate with the pattern of the atmospheric CO₂ curve and probably document temperature and vegetation changes in the regional climate. Recent studies highlighted the influence of temperature and precipitation on $\delta^{13}\text{C}_{\text{wax}}$. Diefendorf et al. (2010) for example demonstrated a strong positive correlation between mean annual precipitation and carbon fractionation in C₃ plants at a global scale. Vogts et al. (2009) found a shift to enriched $\delta^{13}\text{C}_{\text{wax}}$ -values from a C₃ dominated rain forest, where water supply and air humidity are relatively high, over C₃ savanna to C₄ grassland vegetation. Mihailova et al. (2015) investigated long chain *n*-alkanes in olive oils from different Mediterranean countries and found more depleted $^{13}\text{C}_{\text{wax}}$ and $\delta^2\text{H}_{\text{wax}}$ -values in the northern samples compared to the more southern, more arid part. Hence, in the El Paraíso LPS variations in $\delta^{13}\text{C}_{\text{wax}}$ from MIS 4 to MIS 2 were most likely controlled by water availability (i.e. precipitation, relative humidity). The decrease of $\delta^{13}\text{C}_{\text{wax}}$ during MIS 4 indicates a trend to more humid conditions (Fig. 2). Increased aridity is reflected by the more enriched values in deposits related to MIS 3, while a trend to more depleted values again indicates more humid conditions at the transition into the MIS 2.

As the fractionation of $\delta^{13}\text{C}_{\text{wax}}$ in plants not only depends on climate but can also be influenced by a variety of plant-physiological factors (Diefendorf and Freimuth, 2017) we combined the $\delta^{13}\text{C}$ data of the sedimentary leaf wax *n*-alkanes with their $\delta^2\text{H}$ -values to get a more robust and stable insight in paleoclimatic changes and minimize the probability of other than climatic effects on leaf wax fractionation.

4.2. Paleoclimatic interpretation of $\delta^2\text{H}_{\text{wax}}$

The $\delta^2\text{H}_{\text{wax}}$ -values vary constantly over the deposition time of El Paraíso LPS. As in the case of $\delta^{13}\text{C}_{\text{wax}}$, multiple factors may likewise influence $\delta^2\text{H}_{\text{wax}}$ -values (Sachse et al., 2012). A major influence on $\delta^2\text{H}$ -values of leaf waxes arises from changes in $\delta^2\text{H}_{\text{precip}}$ over time. These $\delta^2\text{H}_{\text{precip}}$ changes, in turn, are controlled by changes in the isotopic composition of the moisture source (including changes of the moisture source itself) and thus, changes in the atmospheric circulation systems. To some degree, also temperature and amount effects may influence $\delta^2\text{H}_{\text{precip}}$ changes. Precipitation at our research site is dominated by moisture coming from the North Atlantic (NA) (Moreno et al., 2014a; Roberts et al., 2008) which is related to the strength and position of the westerly storm tracks. During glacial times, oceanic and atmospheric circulation patterns were different compared to interglacial phases. Ice coverage, temperature and variations in salinity led to a more southwards position of the westerlies (Florineth and Schlüchter, 2000) during glacial and hence, to a southward shift of the moisture source. Information about the Late Quaternary NA and Mediterranean surface water isotopic variations comes from $\delta^{18}\text{O}$ records from the planktonic foraminifera *G. bulloides*, offshore Portugal (de Abreu et al., 2003, core MD 95-2040 Fig. 1a).

The $\delta^{18}\text{O}$ record of de Abreu et al. (2003) in Fig. 2 shows that NA surface water became depleted in ^{18}O at the transition from MIS 2 to MIS 1, which is in agreement with the trend to more depleted $\delta^2\text{H}_{\text{wax}}$ values in the El Paraíso LPS in the same time interval (i.e. -147.9‰ to -156.8‰ for *n*-C₃₁, Table 1). A more enriched ^2H during MIS 2 compared to the Holocene is also found in a speleothem record from the Pindal Cave (Moreno et al., 2010), strengthening a pronounced influence of the moisture source on the $\delta^2\text{H}_{\text{wax}}$ composition throughout this time interval. During MIS 3, $\delta^{18}\text{O}$ indicates a tendency towards more depleted values in the marine record that is in agreement with the $\delta^2\text{H}_{\text{wax}}$ curve of the section Paraíso. In the course of MIS 4, $\delta^{18}\text{O}$ values of the NA surface waters indicate a distinct increase that again is

similarly reflected by the $\delta^2\text{H}_{\text{wax}}$ record of the El Paraíso LPS. The relatively positive $\delta^2\text{H}_{\text{wax}}$ values during MIS 5 in the El Paraíso LPS may correlate with positive values in the marine records during MIS 5, although this correlation should be taken with care.

Thus, overall, the variations in $\delta^2\text{H}$ in the El Paraíso LPS correspond with $\delta^{18}\text{O}$ variations of the moisture source. Changes in the atmospheric circulation and the moisture source may very well be responsible for enriched values during MIS 2 and MIS 4 and probably document a more southern NA source area.

The temperature effect, as it is known from Greenland ice cores and speleothems from the Alps (Boch et al., 2011; Moseley et al., 2014) and the northern Iberian Peninsula (Moreno et al., 2010), does not seem to exert a dominant control on isotope signatures of the loess sequence.

4.3. Paleohydrological implications of the δ_{wax} -proxies

The $\delta^{13}\text{C}_{\text{wax}}$ -proxy implies that the cold periods MIS 4 and MIS 2 both are characterized by more humid conditions compared to the warmer phases MIS 3 and the Holocene. This seems to contradict published pollen records (e.g. Carrión et al., 2010; González-Sampériz et al., 2010; González-Sampériz et al., 2006; Valero-Garcés et al., 2004). However, geomorphological records, as well as climate models also indicate more humid conditions during MIS 2 and the global LGM (Beghin et al., 2016; Domínguez-Villar et al., 2013; Moreno et al., 2012, 2014b; Prentice et al., 1992; Valero-Garcés et al., 2004), challenging the pollen results. The results of the vegetation reconstruction based on the *n*-alkane and *n*-alkanoic acid distribution patterns in the El Paraíso LPS also corroborate the δ_{wax} -proxies as they show a higher contribution from deciduous trees and hence, more humid conditions during MIS 2 (Schäfer et al., 2016). Moreover, the contradiction between pollen and other climate proxies is not only known from the Mediterranean (R. Zech et al., 2013), it also arises in other regions during the LGM that are located at similar latitudes and exhibit comparable atmospheric patterns, for example the southern USA (e.g. Menking et al., 2004). As a possible reference, R. Zech et al. (2013) suggested that LPSs might be particularly sensitive archives for arid/humid changes, because they are situated on plateaus and generally more elevated positions, while pollen archives such as lakes and peats are generally located in topographic depressions and hence may be not so sensitive for changes in water availability.

Climate models verify that the atmospheric patterns over Southern Europe were quite different during the LGM than today, and a more southward location of the westerlies resulted in an enhanced seasonal precipitation pattern (Hatté et al., 2013; Sijp and England, 2009 and references therein). More precipitation during winter, when plants were not growing, would have led to higher lake levels, but a pronounced drought during the vegetation period in summer/spring would have resulted in a dominance of steppe vegetation (Florineth and Schlüchter, 2000). This enhanced seasonality pattern might serve as an explanation for the contradiction between pollen records and lake level reconstructions, but it can neither explain that the leaf wax patterns in El Paraíso LPS indicate an increase in deciduous trees during the MIS 2 nor that the δ_{wax} -proxies show more humid conditions in the same time interval. At this point, we do not have an explanation yet why the results of pollen records from the Western Mediterranean disagree with other records. Various studies exist from other regions where pollen records and leaf wax patterns/isotopes are in good agreement (e.g. Schwark et al., 2002; Brincat et al., 2000; Tarasov et al., 2013) and contain often complementary information. Depending on climatic and environmental settings and additional paleoinformation, both paleoproxies, pollen as well as leaf waxes tend to have more or less pronounced uncertainties. The δ_{wax} -proxies can be influenced by a variety of environmental and plant-physiological factors (see Sections 4.1 and 4.2) and it can be challenging to unravel the contribution of all possible parameters (Wirth and Sessions, 2016). However, coupling different proxies such as $\delta^2\text{H}$ and $\delta^{13}\text{C}$ may help to eliminate some uncertainties

(Diefendorf and Freimuth, 2017). Interpretation of pollen records from the last glacial can also be challenging, because modern pollen analogues for glacial steppe vegetation do not exist (Hatté et al., 2013) and the potential impact of a lower atmospheric CO₂ concentration on pollen production during glacials is not well known (González-Sampérez et al., 2010).

Our results and interpretation of the δ_{wax} -record in El Paraíso LPS are supported by other independent proxies from the region, which all together allow doubts on the pollen-based notion of a cold and arid LGM in Central Spain and demand further examination.

5. Conclusions

The δ_{wax} proxies in the El Paraíso LPS reveal Late Quaternary paleohydrological changes in Central Spain.

- Both δ_{wax} -proxies show more humid conditions during the glacial periods MIS 4 and MIS 2 compared to MIS 5, MIS 3 and the Holocene.
- Variations in $\delta^{13}\text{C}_{\text{wax}}$ can be interpreted in terms of changes in water availability for C₃ plants and imply that the (local) climate may have been particularly arid at times during MIS 3.
- A shift to more depleted $\delta^{13}\text{C}$ -values from MIS 2 to the Holocene can be explained with an increase in the atmospheric CO₂ concentration, leading to an increased discrimination against ^{13}C during lipid synthesis and does probably not reflect an increase in humidity. Vegetation reconstruction based on *n*-alkane distributions makes an influence of a changing vegetation composition unlikely.
- $\delta^2\text{H}_{\text{wax}}$ variations correspond to changes in $\delta^{18}\text{O}$ in the North Atlantic surface waters, indicating that the source effect was one dominant control on $\delta^2\text{H}_{\text{wax}}$.

More records from the Western Mediterranean with higher resolution are necessary to validate our interpretation regarding the paleohydrology during the global LGM and the extent of more humid conditions in Central Spain. However, the coupling of $\delta^{13}\text{C}_{\text{wax}}$ and $\delta^2\text{H}_{\text{wax}}$ delivered consistent results and allowed more precise information about paleoclimate and paleoenvironmental changes than one of the δ_{wax} proxies alone. Thus, this study proved the great potential arising from the coupling of $\delta^{13}\text{C}$ and $\delta^2\text{H}$.

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